

UNITED STATES PATENT APPLICATION

FOR

CELLULOSIC PRODUCTS CONTAINING IMPROVED
PERCENTAGE OF CALCIUM CARBONATE FILLER IN THE
PRESENCE OF OTHER PAPERMAKING ADDITIVES

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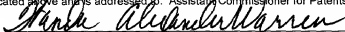
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**CELLULOSIC PRODUCTS CONTAINING IMPROVED
PERCENTAGE OF CALCIUM CARBONATE FILLER IN THE
PRESENCE OF OTHER PAPERMAKING ADDITIVES**

Background of the Invention

1. Brief Description of the Invention

This invention is related generally to cellulosic products, and in particular to such products containing improved percentage of calcium carbonate fillers.

2. Related Art

Cellulose is an essential raw material to make paper. The major sources of cellulose can be grouped into wood, non-wood and recycled fibers. Wood provides about 93% of the world's virgin fiber requirements. One of the challenges during papermaking is to separate the cellulose from components detrimental to papermaking, such as lignin. The process of pulping and bleaching removes much of organic binding material, most of which are lignin, and exposes the fiber for further treatment.

In general, subsequent to pulping and bleaching the fibers are refined. During refining, the fibers are subjected to a mechanical action to develop their optimal papermaking properties with respect to the product made. Overall, during the process of chemical and mechanical separation, the cellulose fibers are modified and degraded. The properties of paper largely depend upon the structure of various fibers that compose the sheets. Also, a wide range of chemicals are known to be used in the papermaking stock furnish to impart or enhance specific sheet properties or to serve other necessary purposes. Chemicals for control purposes, such as drainage aids, defoamers, retention aids, pitch dispersants, slimicides and corrosion inhibitors are added as required based on process and quality requirements.

Calcium carbonate is one of these chemicals added during alkaline papermaking and is included within the classification of "filler". Calcium carbonate is added to fill out spaces between fibers, to improve optical and surface properties of paper, and also to reduce the manufacturing costs. This is because fillers are generally less expensive compared to fibers, with the exception of certain specialty

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pigments. Fiber morphology and calcium carbonate characteristics largely determine calcium carbonate deposition mechanism in the final product.

In discussing fiber morphology, it is essential to consider origination of fiber in wood and transformations to fiber that occur during papermaking. Wood is classified into hard and softwoods. The differences are the result of the development and growth of wood cells. The cells are elongated cells and most are oriented in the longitudinal direction of the stem. The wood substance in soft woods is composed of two different cells: tracheids, also know as fibers, (90-95%) and ray cells (5-10%). Hardwood contains tracheids (55%), vessel elements (30%) with the rest being ray and parenchyma cells. Principal functions of the cells are to a) perform the function of liquid transport; b) provide mechanical strength; and c) food storage. The principal function varies with cell type. The "cell pits" between adjacent wood fibers or cells accomplish the distribution of aqueous solutions and nutrients. J. Gullichsen, H. Paulapuro, *Paper Science and Technology*, Book 3, TAPPI, Ed.2000, page 22. The type of pit depends on the cell type in which the pits are found. The tree grows through the division of cells. The division of cells and growth of the tree are a continuous process, and the growth rate depends upon the species and conditions of the environment.

Regarding fiber morphology, the wall of a typical tracheid or "fiber" is composed of several layers. Tracheids are a long, tapering cell formed essentially in soft woods. When a cell divides, it first develops a cell plate. Each of the two new cells subsequently encloses itself within a thin, extensible, primary wall, consisting of cellulose, hemi-celluloses, pectin, and protein. In summary, the cellulose forms a skeleton, which is surrounded by hemi-cellulose and lignin. During the phase of differentiation, all fibers grow inward from their very thin outer primary wall, successively forming a thin outer boundary (S1) wall, then a thick inner secondary (S2) wall, which is the main body of the fiber, and finally a very thin tertiary (T) wall and a thinner, and usually warty membrane around the lumen.

The S1 and T walls are similar to each other, both being only a fraction of a micron thick. The elements in the S1 wall of a wood fiber are wound spirally in both directions at a very steep angle to the fiber axis, and those in the S2 wall usually have

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a Z winding at a small angle to the fiber access, which angle often increases as the center is approached.

Natural fibers can be split into fibrils that have a width upwards of 0.2 microns. These visible ones are called fibrils and smaller ones down to about 30 nanometers are called microfibrils, and still smaller ones from 30 to about 3 nanometers, it is proposed, should be called nanofibrils. These in turn are bundles of elementary fibrils which are about 35 Angstroms in diameter, each composed of perhaps 16 laterally joined chains of cellulose molecules. (See d'A Clark, James, *Pulp Technology and Treatment for Paper*, Miller Freeman Publications, Ed.1985, page 6.11.)

The process of refining during papermaking effects the partial removal of primary wall. Removal of primary wall exposes the secondary wall for refining. Further refining of secondary wall induces fibrillation and promotes hydration. (See Smook, G.A., *Handbook for Pulp and Paper Technologists*, TAPPI, Ed.1989, page 181). Fibrillation involves loosening of the fibrils that are already present and raising of the finer microfibrils on the surface of the fibers, resulting in very large increase in surface area for the refined fibers.

Typically, the calcium carbonate source is either ground calcium carbonate (GCC) or precipitated calcium carbonate (PCC). GCC is made from grinding the natural product limestone, while PCC is made synthetically outside of the papermaking process. Various types of water-soluble polymers are typically added to retain fillers. Certain polymers are also added to improve water drainage from cellulosic material. In general, all these chemicals are added to improve the runability of the paper machine or the paper quality. Very often, however, excessive use of chemicals leads to problems causing chemical imbalances in the wet end of the paper machine. This negatively impacts runability and paper quality.

With such large variation in fiber morphology and function of these chemicals, it is important to control the quantity and point of addition of these chemicals. A preferred method to monitor and control the chemical imbalances is using charge measurements. Zeta potential is a tool used for charge measurements.

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The current methods of direct addition of calcium carbonate to the pulp or cellulosic fiber have severe drawbacks. The current method is to add calcium carbonate to the cellulosic pulp as a slurry diluted with water either shipped to the mill or made on site. The drawbacks of this are:

- 5 (a) It is difficult to achieve filler content above 20-30% on the final product based on retention aids presently used.
- (b) It results in low levels of single-pass retention. The single-pass retention is expressed as (amount retained in sheet)/(amount from headbox). Low levels of single-pass retention give rise to non-uniform
- 10 distribution of filler particles in the cross-section of the sheets.
- (c) It leads to variations in charge, either positive or negative, depending upon the system, causing charge imbalances.
- (d) Industry demands increased paper machine speeds, minimized wash water usage, and minimized effluent discharge are all limited by the
- 15 need to have an improved filler retention method.

In the last several years, several paper-producing companies have confirmed their interest in the in-situ production of "precipitated calcium carbonate" (PCC), and these companies have either run their own tests or have patented new technologies.

- 20 U.S. Patent No. 4,510,020 describes paper having improved properties produced from pulp in which filler is selectively loaded within the fiber lumen by agitating a suspension of pulp and filler until the fiber lumens become loaded with filler, separating the residual suspended filler from the loaded fibers, and vigorously washing the pulp until substantially all the filler on the external surfaces of the fibers is removed.

- 25 U.S. Patent Nos. 5,275,699 and 5,096,539 describe a process for the in-situ production of fillers from two salts. The salts are combined to precipitate calcium carbonate in the cell wall of fibers and within the fiber itself. The fibers used either can be dried fibers or wet fibers. The fibers can be further washed to remove the calcium carbonate from the exterior of the cell walls.

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U.S. Patent Nos. 5,158,646 and 5,122,230 describe fillers produced by adding a water-soluble inorganic compound to a fiber slurry. The fibers are then pressed so that only the water-soluble compound remains in the fiber wall. The high-consistency fibers are then subjected to a precipitant gas that renders the inorganic compound water-insoluble.

U.S. Patent No. 5,223,090 describes a process for the production of in-situ calcium carbonate, wherein the calcium carbonate is produced by adding calcium oxide or calcium hydroxide to a fiber slurry and subjecting the slurry to high shear mixing while injecting carbon dioxide.

U.S. Patent Nos. 5,731,080 and 5,824,364 describe processes for the production of in-situ calcium carbonate, wherein the processes consist of providing fibers with microfibrils. Calcium ions are then added to the suspension of fibers followed by carbonate ions. This procedure results in a product where most of the calcium carbonate is precipitated and grafted on the microfibrils. This patent claims to provide a product with more than 20% filler.

U.S. Patent No. 5,679,220 describes a method of adding a solution of calcium oxide to a fiber stream and then adding carbon dioxide under light mixing conditions to produce in-situ calcium carbonate. The order of addition of carbon dioxide and calcium oxide can be changed to better control the pH of the slurry. This process is performed at low consistency (less than 5%).

U.S. Patent No. 5,665,205 describes a process of adding an alkaline salt to recycled fibers and then adding a gas to precipitate a filler to improve brightness and cleanliness of the final product.

EP Patent No. 791,685 and World Patent Application W097/01670 describe a procedure for adding a filler to a pulp based on cellulose fibers, characterized in that the pulp is fluidized, whereupon calcium hydroxide is added into it and calcium carbonate is precipitated with carbon dioxide. The '670 document describes precipitation of PCC on fiber fines that are added as a filler.

World Patent Application W099/42657 describes a process of preparing one composition of calcium bicarbonate and one composition of calcium hydroxide,

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followed by mixing of these two compositions in the presence of fibers to produce in-situ calcium carbonate. Also disclosed is a product consisting of unitary crystals grafted on the fibers themselves. Finally, also disclosed is the use of carbon dioxide to dissolve calcium carbonate in waste papers and to remove calcium carbonate from the waste papers.

World Patent Application W001/12899 describes a process of using cellulosic fibers wherein bicarbonates are added, carbonates or silicates of alkaline and alkaline-earth metals (K, Ca, Na, Mg) followed by adding a hydroxide compound to precipitate the silicates or carbonates.

As explained in the above patents, fillers are typically added during papermaking to improve the quality of final product. The addition of calcium carbonate as a filler improves optical properties of the paper and also reduces the amount of expensive fiber required for making paper. A typical content of calcium carbonate in white coated (or) uncoated paper grades is in the range of 20-30%. The calcium carbonate is either obtained as ground calcium carbonate (GCC) or precipitated on-site, so-called precipitated calcium carbonate, or PCC. In order to contain the calcium carbonate in paper, polymeric compounds are frequently used as retention aids.

As explained above in reference to World Patent W099/42657, one alternate method to prepare calcium carbonate is by in-situ deposition on the fibers or in the fibers, where the in-situ PCC is prepared by mixing the reactants necessary to form calcium carbonate directly with the fiber pulp. One such method, as explained in the '657 patent document, is by using calcium carbonate as one of the reactants, along with lime and carbon dioxide.

It would be preferred if an improved method of in-situ calcium carbonate deposition could be conceived. Calcium carbonate present in known papermaking methods, including known in-situ precipitation methods, tends to be uniformly distributed inside and outside the fiber lumen. Furthermore, the trend is to avoid binders and retention aids.

In all of the above methods, there was a desire to increase calcium carbonate in the final sheet of paper greater than 20 weight percent and also to eliminate the use

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of retention aids. For example, in U.S. Patent No. 5,824,364, the calcium carbonate crystals are disclosed as being directly grafted to microfibrils as granules without binders and retention aids present at the interface between the microfibrils and the granules. Also, the precipitated calcium carbonate is uniformly distributed when
5 directly grafting to the microfibrils. The majority of protocols trap the microfibrils by reliable and non-labile mechanical binding. The surface area of the fiber as defined by the inventors is a function of the number of microfibrils. The surface area of the fibers of the composite is in the range of 3-200 square meters per gram. The calcium carbonate contained in the sheet is limited to the available microfibrils surface area, as
10 specified by the inventors in the range of 3-200 square meters per gram, and which can also significantly vary depending on the fiber source.

In the above-mentioned U.S. Patent No. 4,510,020, the calcium carbonate is prepared within the fiber lumens until the fiber lumens become loaded with fiber and further washing is used to remove substantially all of the filler on the external surfaces
15 of the fibers, including microfibrils. In case of fibrillated pulps, considerable difficulty is experienced in removing the filler from the fibrillated external surfaces. The inventors also indicated that it is possible to produce fibrils by prolonged beating, described as "fine fuzz". The inventors also disclosed that fibrillated pulps, such as highly-beaten chemical pulps, and most mechanical pulps, pose a problem to their
20 invention. The fibrillated external surfaces tenaciously hold pigments throughout the washing treatment. Furthermore, as explained by the inventors, there can be instances when the lumen can be collapsed, limiting the accessibility for calcium carbonate precipitation due to severe pressing or drying. The fibrillated pulp can compete for calcium carbonate, thereby minimizing the availability inside the lumen.

25 U.S. Patent No. 4,892,590 explains a method of using separately prepared calcium carbonate and a cationic starch for improving filler retention, opacity and strength during papermaking.

All of the above prior art methods achieve high filler retention by focusing on individual sections of the fiber, such as in the lumen, cell wall, or microfibrils. The
30 overall calcium carbonate contained in the final sheet is limited to the availability and surface area of these individual sections. The calcium carbonate contained in the paper sheet using the prior art methods is prepared without using retention aids or

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binders. The methods require controlled conditions to achieve the presence of calcium carbonate in the targeted sites.

Summary of the Invention

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5 In accordance with the present invention, cellulosic products are prepared using methods significantly different from the prior art, resulting in cellulosic products that are different from the prior art. The cellulosic products of the present invention contain calcium carbonate in all available areas of a fiber, and not constrained to a single location as in the prior art. The formation of calcium carbonate is found to be random (non-uniform) in relation to size, shape, location and
10 crystal morphology. During paper production, non-saleable paper is reused, which is generally known within the industry as "broke." The non-saleable paper originates during papermaking before drying, or after drying but before reeling, or after drying and reeling. The amount of broke addition can vary, depending upon operating conditions and preference. Since the broke is already paper, it contains all the
15 chemicals that are added during the papermaking process. The broke is an essential part of the papermaking process, which cannot be ignored. These "broke chemicals" are expected to interfere and interact in calcium carbonate formation to provide a chemical bonding between the fiber and the calcium carbonate. It's also valid in case of mills using recycled paper for example mixed office waste as a portion of the furnish. Similar to the broke the recycled paper contains chemicals and additives used
20 during papermaking before being recycled.

In accordance with the present invention, cellulosic products containing improved percentages of calcium carbonate are described. The products of the invention are characterized by non-uniformly distributed calcium carbonate in and
25 around the fiber structure, inside lumen, cell wall, microfibrils, deposited in pits, and outside of the lumen. In other words it is possible by using the techniques of the invention to produce cellulosic products having all available real estate available in a fiber for containing calcium carbonate, that is, the entire surface area. Furthermore, since the processes used to produce the cellulosic products of the invention are
30 positioned within a papermaking machine wet end, the calcium carbonate and fibers will interact with chemicals typically used in paper making producing chemical bonding between calcium carbonate and cellulose chemical structure. By the

techniques of the invention, the cellulosic products of the invention have improved calcium carbonate addition, the improved addition occurring during the paper making process.

As used herein "papermaking process" means conditions that exist within the
5 fiber mass during formation of a sheet of paper. In commercial sheet forming paper machines, there are three elementary forming operations: dilution, turbulence, and oriented shear, all of which are applied in different degrees in an attempt to optimize the final sheet quality. (See G.A. Smook, Handbook for Pulp and Paper Technologists, TAPPI, Ed.1989, page 219.) Substantial binding energy is expected
10 between chemicals added to the fiber and between the fibers itself so that the fibers do not break loose due to these forces during basic sheet forming processes.

Cellulosic products of the invention comprising PCC prepared in-situ during papermaking are prepared by mixing a bicarbonate with lime and with diluted pulp containing fibers, wherein the precipitated calcium carbonate is positioned in the final
15 product in a non-uniform manner on all physical locations of the fiber either as single crystals, agglomerates of crystals, combined agglomerates of crystals, amorphous powders, or combinations thereof. The PCC crystals are contained in the sheet with other various chemical residues used in papermaking, and wherein a majority of PCC is attached to the fiber surface based on chemical bonding, and the PCC comprises at
20 least 15% by weight based on total solids of the cellulosic product, more preferably at least 40%.

Preferred products of the invention are those wherein the zeta potential during papermaking ranges from -5 to about +5, more preferably the zeta potential of the
25 papermaking process ranges from about -2 to about +2, and more preferably is zero. Considerable deviations in zeta potential from zero affect the production and quality of cellulose products. The retention of calcium carbonate on pulp fibers is also affected (negatively) by deviations from zero zeta potential.

30 Also preferred for making paper products of the invention, the freeness of the diluted pulp ranges from about 300 csf to about 900 csf, more preferably ranging from about 400 csf to about 500 csf. In order to produce a pulp of certain freeness, the pulp

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is either beaten or refined using a special mechanical device. Canadian Standard Freeness (csf) is one of the measures used to control freeness. The terms "beating" and "refining" are used interchangeably in the art and herein. The process of refining increases surface area of the fiber and also the amount of water retained by pulp
5 fibers. This also contributes to higher PCC loading of the final product. Extending the process of refining beyond a certain optimum decreases the product quality and paper production.

The products of the invention preferably have PCC crystals having size
10 ranging from about 0.1 micrometer to about 10 micrometers, and the fibers are derived from material selected from the group consisting of wood, non-wood (for example bagasse, nut shells, corn cobs), recycled cellulosic materials, and mixtures thereof. It is also possible, in preferred embodiments, for the products of the
15 invention to include other components, such as glass particles, organic or inorganic pigments, coatings and the like, although these are optional only. See for example d'A Clark, James, Pulp Technology and Treatment for Paper, Miller Freeman Publications, Ed.1985.

The products of the invention preferably employ chemical residues selected
20 from the group consisting of retention aids, flocculants, drainage aids, resins, dispersants, chelants, scale inhibitors, corrosion inhibitors, and slimeicides.

Other preferred products of the invention are those derived from diluted fiber aqueous suspensions having a consistency ranging from about 0.05 percent to about
25 50 percent, more preferably ranging from about 5 percent to about 10 percent.

Preferred cellulosic products of the invention include building products and paper products. Preferably the fibers in the inventive products are bleached fibers, preferably derived from a kraft process. The products of the invention preferably
30 have PCC morphology selected from the group consisting of amorphous, crystalline, powder, and mixtures thereof. If crystalline, it has a crystal morphology selected from the group consisting of calcite, aragonite, vaterite, rhombohedral, sclenohedral, prismatic, and mixtures thereof.

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Brief Description of the Drawings

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FIGs. 10-11 are scanning electron micrographs of calcium carbonate deposited in pits of fibers of products of the invention; and

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Description of Preferred Embodiments

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- secondary cell wall 6 at 22, on an outer surface of fiber 2 at 24, and on fibrils 25 at 26. Fibrils 25 are exposed and raised during refining, where a portion of primary cell wall is removed, exposing secondary wall 6 and its attendant fibrils. Microfibrils raised during refining, not shown, also have PCC deposited thereon. The PCC is preferably deposited as single crystals as illustrated at 24, combined crystals as at 27, and as agglomerates of combined crystals as indicated at 28.

FIGs. 2-11 are scanning electron microscope (SEM) photos of products of the invention, which are further explained in the following examples.

Examples

10 Examples 1-10

- The fibers in each of Examples 1-10, shown in images of FIGs. 2-11, were 50% hardwood, 50% softwood, each refined to 300 CSF using a laboratory fibrillation device known under the trade designation "Valley Beater", Serial No. 109-F-1093 made by Valley Iron Works, Appleton, WI, and available from Testing Machines Incorporated. Testing was performed according to the standard TAPPI Test Method, T-200&SP-96 performed by Econotech Services Ltd., Delta, BC, Canada.

Preparation:

- The samples for all examples were prepared through measured addition of chemicals that are documented to form CaCO_3 precipitate, and the final pH ensured that the reactions were complete. All reactions were performed in the presence of fiber – hence the precipitation was in-situ.

- The fibers in all the images of FIGs. 2-11 were produced by mixing the pulp prepared as above and a CO_3^{2-} ion-containing reagent to fiber consistency of 8.4% in water, using a laboratory mixing device known under the trade designation "Lightin Mixer", available from Lightin, Rochester, NY. The CO_3^{2-} ion-containing reagent was sodium bicarbonate obtained from Arm & Hammer, Princeton, NJ.

Then a Ca^{2+} ion-containing reagent was blended in to provide a fiber consistency of 2.5% for FIGs. 2-7, and a fiber consistency of 5.6% for FIGs. 8-11.

The Ca^{2+} ion-containing reagent in each example was calcium hydroxide $\text{Ca}(\text{OH})_2$, obtained as 95% from Aldrich Chemical Company, Milwaukee, WI.

Gaseous CO_2 was then introduced in each example at atmospheric pressure to reduce the pH of each example to 7.5.

5 For each of Examples 8-11, a second portion of the same Ca^{2+} ion-containing reagent was blended in to provide a fiber consistency of 4.1%, and then gaseous CO_2 was again added at atmospheric pressure to lower the pH to 7.0. The Ca^{2+} was added in two portions to a) minimize Na^+ levels, b) to obtain benefits of two step addition of Ca^{2+} , and c) to achieve in-situ preparation of CO_3^{2-} from hydroxide.

10 Hand sheets were prepared according to TAPPI standard T205 om-88 for all examples. The sheets were subject to an ash test, TAPPI standard T211, wherein the inorganic portion was quantified. This inorganic portion was identified as carbonate by reacting the ash with HCl and measuring the CO_2 evolved on a gas chromatograph.

15 Scanning Electron Microscope Particulars

The scanning electron microscope (SEM) has the capability of performing qualitative elemental analysis using energy dispersive spectroscopy (EDS). This analysis was performed on a particle present on the sample in FIGs. 8, 9, 10, and 11. This analysis yielded only calcium, carbon, and oxygen.

20 The SEM used is known under the trade designation "1600 Turbo Scanning Electron Microscope", available from Amray Corporation, serial number AMR16014008. Also used was a digital spectrometer known under the trade designation "Prism Digital Spectrometer", available from Princeton Gamma Tech (PGT), model number TN1/389140, serial number 52439. This spectrometer
25 employed an X-ray detector known under the trade designation "Pioneer", from Noran Corporation, which was upgraded by PGT to perform digital pulse processing, and fitted with an ultra-thin lithium-beryllium window.

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Analyzer Workstation

The analyzer workstation used was known under the trade designation "IMIX-PC" Analyzer Workstation, available from PGT, and comprised a computer with the following features:

- 5 64MB memory
- 32-bit, 200MHz clock speed
- Windows NT workstation
- Windows NT operating system
- Windows 95 windowing system
- 10 Mass storage: 2 Gbyte disk drive, 1 Gbyte tape drive, 1.44 Mbyte floppy,
- CD- ROM
- 3 button mouse, Windows 95 keyboard
- 17 inch monitor
- Ethernet card.
- 15 This workstation utilized data acquisition hardware available from PGT, serial number 61619, including M427 digitalpulse processing electronics, detector bias supply with integral LN monitor for auto shut-off/turn-on, and a beam driving/image capture subsystem, which included a software package known under the trade designation "IMIX-PC" Software Package, which included:
- 20 X-ray collection and analysis package
- Position Tagged Spectrometry (PTS) package
- Imaging, Mapping, and Beam Control package
- High-resolution SEM Imaging package.

All samples were sputter-coated using a gold target with approximately 367 Angstroms of gold, using a sputter coater known under the trade designation "SPI-Module Sputter Coater", Model number 11430, serial number 001683, and a sputter control module known under the trade designation "SPI-Module Control Unit", Model number 11425, serial number 001682.

Zeta potential measurement procedure

The samples in FIGs 2-11 were oven-dried and stored in separate plastic bags for 7 (seven) months. The plastic bags were polyethylene bags having a coating of material known under the trade designation Saran thereon. The paper samples were then re-pulped in de-ionized water using a 250 ml kitchen blender. The re-pulped finer consistency was 0.5%. The System Zeta Potential (SZP) was measured on the samples using a proprietary instrument known under the trade designation "Mutek SZP-06", available from BTG Industries, Norcross, GA.

Measurement results are detailed in Table 1.

Table 1. Example Results

	Ex 1	Ex 2	Ex 3	Ex 4	Ex 5	Ex 6	Ex 7	Ex 8	Ex 9	Ex 10
FIG. Number	2	3	4	5	6	7	8	9	10	11
filler wt. %	23.0	13.1	23.0	23.0	23.0	14.8	19.3	19.3	19.3	19.3
Zeta potential	-97.6	-97.8	-97.6	-97.6	-97.6	-101.6	-95.8	-95.8	-95.8	-----
SEM magnification	6500x	6500x	14,700x	1000x	6500x	6500x	6500x	3000x	6500x	10,000x
SEM width (microns)	23	23	11	-----	23	23	23	49	23	15

FIGs. 9-11 show PCC deposited in pits. Notice in FIGs 2-11 that the PCC is distributed non-uniformly, and at all available areas, instead of in one particular physical location in the fibers. Also notice the different morphologies of the PCC, for example in FIG. 9. This figure illustrates a large agglomerate of PCC on the left side of the photo, and smaller combinations in the pits. On the other hand, FIG. 10

illustrates an agglomerate in a pit. In general, agglomerates of PCC in products of the invention are located inside pits, attached to fibrils (also microfibrils), and the surface of the fiber itself. The observed calcium carbonate on fiber was singular and at times combined with one another. The distribution of calcium carbonate appeared to vary
 5 with one pit containing significantly more compared to another. Thus, the crystal size, shape and distribution differ and are not consistent from one location to another.

Products of the invention preferably include one or more chemical residues selected from the group consisting of retention aids, flocculants, drainage aids, resins, dispersants, chelants, scale inhibitors, corrosion inhibitors, slimicides, and the like.
 10 These chemical residues help bind at least a portion of the PCC to available surface area on and in the fibers, in the pits, inside the lumens, and the like. A representative listing of suitable chemicals are listed in Table 2. Note that in many cases a combination one two or more of the different chemicals are used, for example, blends of two or more slimicides, so as to inhibit or kill over a broad spectrum.

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Table 2. Suitable Chemical Residues

	Sizing compositions
	internal sizes
	external sizes
20	rosins (colophony), typically fatty organic acids, such as abietic acid rosin soaps (for example sodium abietate)
	starch sizes
	cereal starch (corn, wheat)
	tuber starch (for example potatoe, tapioca)
25	unmodified starches
	modified starches
	oxidized starches
	starch ethers
	cationic starches
30	anionic starches
	amphoteric starches
	starch esters
	hydrophobic starches

acid modified starches
hydrolyzed starches

Alkaline (neutral) sizes

- 5 alkyl ketene dimer (AKD)
 alkenyl succinic anhydride (ASA)
 neutral rosin sizes

Other sizing materials

- wax (either paraffin or microcrystalline)
10 fluorochemicals
 dry strength resins (such as styrene-acrylate copolymers,
 styrene-maleic anhydride copolymers, polyacryamides,
 polyurethanes, and polyvinyl alcohols)

- 15 Cationic Flocculants

 alum (papermakers alum), and alum substitutes such as polyaluminum
 chloride, polyaluminum hydroxychloride, and polyaluminum
 silicate sulfate

- 20 Dyes

 acid dyes, typically used with a dye fixing agent
 basic dyes
 direct dyes
 pigment dispersions

- 25 liquid sulfur dyes

Optical brightening agents (OBA)

 diaminostilbene disulfonic acid derivatives

- 30 OBA quenchers

 quaternary polyamides

Retention aids, drainage aids

 single polymer systems

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- polyacrylamides
polydiallyldimethylammonium chloride
polyethyleneimine
acrylic acid/acrylamide copolymers
- 5 dual polymer systems
a low molecular weight polyamine plus a high molecular
weight polyacrylamide
a polyethylene oxide plus a phenol formaldehyde resin
microparticle retention systems
- 10 bentonites
silica
enzymes
- Wet strength resins
- 15 urea-formaldehyde resins
melamine formaldehyde resins
polyamide-epichlorohydrin resins
polyamino-epichlorohydrin resins
- 20 Wet strength repulping aids (for broke)
peroxodipersulfates
peroxymonosulfate
- Dispersants
- 25 Dialkyl dimethyl quaternary ammonium compounds
Diimido alkoxylated quaternary ammonium compounds
Imidazolone quaternary ammonium compounds
Dialkyl phenoethoxylated quaternary ammonium compounds
- 30 Deposit control agents
detackifiers (for example zirconium compounds)
dispersants
adsorbents (for example talc, bentonite, modified kaolin)
stabilizers (for example, mixtures of clays and zeolites with long chain

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- organic cations)
fixatives (for example polyamines, polyethyleneimines,
polyacrylamides)
enzymes (for example lipases)
- 5 Scale inhibitors, such as paraffin emulsions and terpene emulsions
- Antislimes (slimicides, algicides, antimicrobials, bactericides, biocides
fungicides, biodispersants)
- 10 oxidizers (for example chlorine, bromine, chlorine dioxide, hydrogen
peroxide)
organobromines, organosulfurs, isothiazolinones, thiocyanates
sulfone
glutaraldehyde
- 15 2,2-dibromo-3-nitrilopropionamide
quaternary ammonium compounds
dodecylguanidine hydrochloride
thione (tetrahydro-3,5-dimethyl-2H-1,3,5-thiadiazine-2-thione)
isothiazolin
- 20 benzisothiazolin
biodispersants
ethylene oxide/propylene oxide copolymers
anionic lignosulfonates
enzymes (glucanase enzymes, amylase enzymes, protease
enzymes)
- 25 Antifoams and defoamers
Mineral-oil based
Water emulsions of fats and waxes
Polymeric antifoams (for example silicones, polyethylene glycols, fatty
acid esters)
- 30 Chelants
EDTA (ethylenediaminetetraacetic acid)
DTPA (diethylenetriaminepentaacetic acid)

Corrosion Inhibitors: Inhibitors used in practice are seldom-pure substances, but are usually mixtures that may be byproducts, for example, of some industrial chemical processes for which the active constituent is not known. Commercial inhibitor packages may contain, in addition to the active ingredients for inhibition, other chemicals, including surfactants, deemulsifiers, carriers and biocides. The active ingredients of organic inhibitors invariably contain one or more functional groups containing one or more hetero atoms, N, O, S, P, or Se through which the inhibitors are attached to a parent chain (backbone), which increases the ability of the inhibitor molecule to cover a large surface area. Common repeating units of the parent chain are methyl and phenyl groups. (R. Winston Revive, UHLIG'S Corrosion Handbook, John Wiley & Sons, Inc., 2000, page no. 1097.)

Methods of Preparation of Cellulosic Products

Preferred methods of preparing the cellulosic product of the invention including in-situ precipitated calcium carbonate, a reagent comprising calcium cation (Ca^{2+}) and a reagent comprising the carbonate anion (CO_3^{2-}) are acquired. The source of these ions can be derived from several sources available either in solid, liquid, or gaseous form. One preferred method is to prepare calcium carbonate by using lime and bicarbonate salt. The bicarbonate is preferably originated from several sources, for example they can be either purchased or made onsite. Two examples include the reaction of calcium carbonate with carbon dioxide at a pH of about 8.4, which should produce sufficient bicarbonate ions and solution, and the reaction between sodium bicarbonate and lime.

The inventors herein prefer to use one of several process configurations to deposit in-situ PCC. For example, the methods described in the previously mentioned world patent WO99/42657, incorporated by reference, as one preferred method. Five other preferred methods are those indicated in FIGs. 12-16. For example, FIG. 12 illustrates schematically a process entitled "iPCC alternative one", wherein fibers are mixed with calcium carbonate and carbon dioxide in a first mixer, and then calcium hydroxide is added to the mixture in a second shearing operation. This method comprises the steps of preparing a first slurry of calcium hydroxide having a solids content of at least 15 weight percent and preparing a second slurry of fibers having a

solid content varying between about 3 to about 6 percent by weight. Adding calcium carbonate to the second slurry in an amount equal to about 0.5 weight percent to form a third slurry and another step, and introducing carbon dioxide inset third slurry under a pressure to form a fourth slurry is a fourth step. Adjusting the carbon dioxide addition to an amount equal to the stoichiometric requirement of the calcium hydroxide present in the first slurry so that the end pH is within a range of from about 7.5 to about 8.5 once the first and fourth slurries are mixed together is preferred. Also preferred is agitating the fourth slurry in order to completely solubilize carbon dioxide and to partially solubilize calcium carbonate to form calcium bicarbonate. Finally, having first and fourth slurry under light mixing conditions, such as by using an in-line mixer, this preferred to form a homogeneous slurry of calcium carbonate precipitated physically attached to the fibers.

A second method of forming the product of the invention, described as "iPCC with simultaneous addition of chemicals", is illustrated in FIG. 13. This is a slight modification of the process of FIG. 12, and comprises a step of preparing a first slurry of calcium hydroxide having a salt content of at least 15 weight percent; preparing a second slurry of fibers having a solid content varying between about 3 percent and 6 percent by weight; preparing a third slurry consisting of about 0.5 percent by weight calcium carbonate and carbon dioxide under pressure; and adjusting the carbon dioxide addition to an amount equal to the stoichiometric requirement of the calcium hydroxide present in the first slurry so that the end pH is between about 7.5 to about 8.5 when the three slurries are mixed together. Finally the third slurry is agitated in order to completely solubilize carbon dioxide and to partially solubilize calcium hydroxide to form calcium bicarbonate. Adding the first, second and third slurries under light mixing conditions, such as using an in-line mixer, promotes the formation of a homogeneous slurry of calcium carbonate precipitate physically attached to the fibers.

A variation of the process of FIG. 12, denoted "iPCC alternative with non-gaseous CO₂" is another alternative, and is depicted in FIG. 16. FIG. 16 illustrates mixing of calcium carbonate and carbon dioxide prior to mixing with fiber slurry, thus allowing a bicarbonate-containing solution to be mixed with the fiber slurry.

A fourth process to form the cellulosic products of the invention is illustrated in FIG. 14, denoted "iPCC with fractionation." As illustrated schematically in FIG. 14, this process embodiment comprises first preparing a slurry of low strength contribution fibers and subjecting this slurry of low strength contribution fibers to a calcium carbonate in-situ precipitation process such that the calcium carbonate is physically attached to the low strength contribution fibers. The low strength contribution fibers having PCC attached are then mixed with high strength contribution fibers in a ratio that preferably imparts desired obstacle and strength properties to the final cellulosic product. The amount of calcium added to the low strength contribution fibers is preferably an amount sufficient to reach the desired amount of filler in the end cellulosic product.

FIG. 15 illustrates a fifth method of producing the cellulosic products of the invention, which is named "iPCC with layering." This method comprises first preparing a slurry of low strength contribution fibers and subjecting the slurry to a calcium carbonate in-situ precipitation process, again so that the calcium carbonate is physically attached to the low strength contribution fibers. A second slurry of high strength contribution fibers is prepared, and using the first and second slurries, in a multi-ply paper machine, to produce a paper having high smoothness, high brightness and high strength properties. The multi-ply paper product being formed of to external layers comprising short fibers with physically attached filler which imparts high brightness and smoothness to the surface is formed, with an interlayer consisting of the long, high strength fibers, giving high strength to the paper. The amount of calcium added to the low strength contribution fibers is preferably an amount sufficient to reach the desired amount of filler in the end cellulosic product.

As said previously one major benefit of the practice of the present invention is the utilization of the entire real estate, that is, all available surface area, in and around the fibers for maximum deposition of calcium carbonate fillers. One limitation of the present invention is that it is difficult to preferentially control deposition within a certain section of the fiber. However, this is compensated by the fact that the present method is less expensive and easier to implement.

In order to facilitate calcium carbonate formation a reactant containing calcium ions (Ca^{2+}) is preferably brought into contact with another reactant capable

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of producing carbonate ions (CO_3^{2-}). In practicing the preferred methods of forming the cellulosic products of the invention, any one of the reactant may be either positively or negatively charged, and is initially dissolved in the pulp slurry. Since the pulp will contain sufficient amount of water, this enables migration of the charged ions in and around the entire cross section and all available areas of the fiber. The behavior of ion transportation inside the fiber, especially in the lumen, can be compared to a straw in a cup of water. Residence time, mixing, and temperature of the system are a few variables that can be used to control the solubility and migration of ions within the pulp fibers. Increase of one or more of these three parameters will tend to increase the amount of ion transportation. Once sufficient migration of ions has taken place, counter ions are introduced to facilitate precipitation. Again, this can be accomplished by adjusting any of the variables, such as residence time, mixing, and temperature of the system, and again, increase in any one or more of these parameters will tend to increase counter ion migration and eventual reaction of counter ion with ions. This should in general increase the quantity of calcium carbonate deposited or precipitated on pulp fibers. And as can thus be seen, the methods used to produce the products of the present invention are not selective to any one section or location of the fiber in precipitating calcium carbonate.

In the art of making paper, it is well known that the presence of calcium carbonate causes scale formation in pulping and papermaking equipment. A major source of calcium for this scale formation originates as a nutrient from water and is stored within the fiber structure. When reactants capable of producing carbonate ion are introduced, some of these free calcium ions in the fiber are likely to react to form calcium carbonate as well. The amount of calcium carbonate formed due to this phenomenon is dependent upon the species, processes, water quality, and the like.

The in-situ calcium carbonate formation is predominately governed by the conditions that exist within the wet papermaking end of a papermaking process, compared to other synthetic methods of preparing calcium carbonate. In in-situ processes such as used to make the products of the present invention, calcium carbonate is formed in the presence of pulp fibers by mixing reactants with the pulp slurry. This fact ensures that there are fewer opportunities to adjust the calcium

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carbonate characteristics or its location within the fiber structure, which is an important aspect of the present invention.

5 Filler particles can be entrapped "mechanically" into the fiber web, or "chemically", aided by chemical additives (polymers). In practice, preferably as good retention of calcium carbonate as possible is of course desirable, although other paper properties and process conditions must also be taken into account. Mechanical entrapment of filler particles is very low before the formation of a fiber mat where filtration can take place. After formation of a fiber mat, entrapment of fillers is a size-dependent mechanism, with retention increasing with increasing particle size. By the introduction of chemical additives, the retention can be improved considerably.

15 With regard to paper making, it is never just a combination of calcium carbonate and fiber. Several other chemicals need to be added during paper making in order to improve production and quality. The interaction is between the chemicals added generally referred to as processing aides (for example wet strength additives, sizing, slime control, drainage aides, dyes, dispersants, and the like), residual chemicals from earlier treatments, calcium carbonate and fiber will all predominantly influence the mechanism by which calcium carbonate is attached to pulp fibers. Under these circumstances, while it is difficult to prove positively, the inventors herein maintain that there is significant chemical attachment at the particle/fiber interface as compared to mechanical bonding alone. To meet the requirements of both ecology and economy, the reusable fibers and processing aide chemicals are reclaimed and recirculated into the machine furnish further enhancing chemical bonding.

25 Although the above description of preferred products of the invention, and methods of making same, are representative of the invention, they are by no means intended to limit the scope of the appended claims.

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